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(54) Food freezing method using a multicomponent refrigerant

(57) A method for providing refrigeration, such as to an insulated enclosure for food freezing, wherein a defined hydrocarbon-containing multicomponent refrigerant fluid undergoes a phase change coupled with Joule-Thomson expansion to generate refrigeration over a wide temperature range which may comprise from ambient to low temperatures.

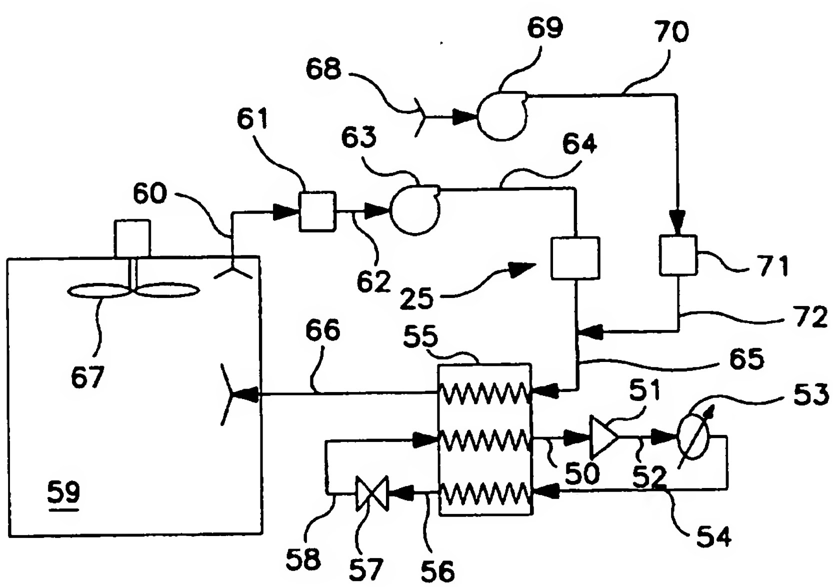

FIG. 1

(C_7H_{16}), ethylene (C_2H_4), propylene (C_3H_6), butylene (C_4H_8), hydrogen (H_2), methanol (CH_3OH), ethanol (C_2H_5OH), i-propanol (i-C_3H_7OH), n-propanol (n-C_3H_7OH), i-butanol (i-C_4H_9OH), n-butanol (n-C_4H_9OH), 2,2-dimethyl propane ($(CH_3)_4$-C), 2,3-dimethyl butane ($(CH_3)_2CHCH(CH_3)_2$), 2,2-dimethyl butane ($CH_3CH_2C(CH_3)_3$), 2-methyl pentane ($C_3H_7CH(CH_3)_2$) and 3-ethyl pentane ($(C_2H_5)_2CHCH_3$).

[0018] As used herein the term "fluorocarbon" means one of the following: tetrafluoromethane (CF_4), perfluoroethane (C_2F_6), perfluoropropane (C_3F_8), perfluorobutane (C_4F_{10}), perfluoropentane (C_5F_{12}), perfluoroethene (C_2F_4), perfluoropropene (C_3F_6), perfluorobutene (C_4F_8), perfluoropentene (C_5F_{10}), hexafluorocyclopropane (cyclo-C_3F_6), octafluorocyclobutane (cyclo-C_4F_8) and perfluorohexane (C_6F_{14}).

[0019] As used herein the term "hydrofluorocarbon" means one of the following: fluoroform (CHF_3), pentafluoroethane (C_2HF_5), tetrafluoroethane ($C_2H_2F_4$), heptafluoropropane (C_3HF_7), hexafluoropropane ($C_3H_2F_6$), pentafluoropropane ($C_3H_3F_5$), tetrafluoropropane ($C_3H_4F_4$), nonafluorobutane (C_4HF_9), octafluorobutane ($C_4H_2F_8$), undecafluoropentane (C_5HF_{11}), methyl fluoride (CH_3F), difluoromethane (CH_2F_2), ethyl fluoride (C_2H_5F), difluoroethane ($C_2H_4F_2$), trifluoroethane ($C_2H_3F_3$), difluoroethene ($C_2H_2F_2$), trifluoroethene (C_2HF_3), fluoroethene (C_2H_3F), pentafluoropropene (C_3HF_5), tetrafluoropropene ($C_3H_2F_4$), trifluoropropene ($C_3H_3F_3$), difluoropropene ($C_3H_4F_2$), heptafluorobutene (C_4HF_7), hexafluorobutene ($C_4H_2F_6$), nonafluoropentene (C_5HF_9), decafluoropentane ($C_5H_2F_{10}$), undecafluoropentane (C_5HF_{11}), hexafluorobutane ($C_4H_4F_6$) and pentafluorobutane ($C_4H_5F_5$).

[0020] As used herein the term "fluoroether" means one of the following: trifluoromethyoxy-perfluoromethane (CF_3-0-CF_3), difluoromethoxy-perfluoromethane (CHF_2-O-CF_3), fluoromethoxy-perfluoromethane (CH_2F-O-CF_3), difluoromethoxy-difluoromethane (CHF_2-O-CHF_2), difluoromethoxy-perfluoroethane (CHF_2-O-C_2F_5), difluoromethoxy-1,2,2,2-tetrafluoroethane (CHF_2-O-C_2HF_4), difluoromethoxy-1,1,2,2-tetrafluoroethane (CHF_2-O-C_2HF_4), perfluoroethoxy-fluoromethane (C_2F_5-O-CH_2F), perfluoromethoxy-1,1,2-trifluoroethane (CF_3-O-$C_2H_2F_3$), perfluoromethoxy-1,2,2-trifluoroethane (CF_3O-$C_2H_2F_3$), cyclo-1,1,2,2-tetrafluoropropylether (cyclo-$C_3H_2F_4$-O-), cyclo-1,1,3,3-tetrafluoropropylether (cyclo-$C_3H_2F_4$-O-), perfluoromethoxy-1,1,2,2-tetrafluoroethane (CF_3-O-C2HF4), cyclo-1,1,2,3,3-pentafluoropropylether (cyclo-C_3H_5-O-), perfluoromethoxy-perfluoroacetone (CF_3-O-CF_2-O-CF_3), perfluoromethoxy-perfluoroethane (CF_3-O-C_2F_5), perfluoromethoxy-1,2,2,2-tetrafluoroethane (CF_3-O-C_2HF_4), perfluoromethoxy-2,2,2-trifluoroethane (CF_3-O-$C_2H_2F_3$), cyclo-perfluoromethoxy-perfluoroacetone (cyclo-CF_2-O-CF_2-O-CF_2-), cyclo-perfluoropropylether (cyclo-C_3F_6-O), methoxy-perfluoromethane (CF_3-O-CH_3), methoxy-perfluoroethane (C_2F_5-O-CH_3), methoxy-perfluoropropane (C_3F_7-O-CH_3), methoxy-perfluorobutane (C_4F_9-O-CH_3), ethoxy-perfluoromethane (CF_3-O-C_2F_5), ethoxy-perfluoroethane (C_2F_5-O-C_2F_5), ethoxy-perfluoropropane (C_3F_7-O-C_2F_5), ethoxy-perfluorobutane (C_4F_9-O-C_2F_5).

[0021] As used herein the term "atmospheric gas" means one of the following: nitrogen (N_2), argon (Ar), krypton (Kr), xenon (Xe), neon (Ne), carbon dioxide (CO_2), oxygen (O_2), helium (He) and nitrous oxide (N_2O).

[0022] As used herein the term "low-ozone-depleting" means having an ozone depleting potential less than 0.15 as defined by the Montreal Protocol convention wherein dichlorofluoromethane (CCl_2F_2) has an ozone depleting potential of 1.0.

Brief Description Of The Drawings

[0023]

Figure 1 is a schematic flow diagram of one preferred embodiment of the multicomponent refrigerant refrigeration system of this invention.

Figure 2 is a schematic flow diagram of another preferred embodiment of the multicomponent refrigerant refrigeration system of this invention.

Figure 3 is a schematic flow diagram of another preferred embodiment of the invention wherein multiple level refrigeration is provided.

Figure 4 is a schematic flow diagram of another preferred embodiment of the invention wherein multiple level refrigeration is provided and there is more than one phase separation.

Figure 5 is a schematic flow diagram of another preferred embodiment of the invention for use with multiple enclosures.

Detailed Description

[0024] The invention comprises, in general, the use of a defined hydrocarbon-containing zeotropic mixed refrigerant to efficiently provide refrigeration over a large temperature range, such as from ambient temperature to a low temperature. The refrigeration may be employed to provide refrigeration directly or indirectly to one or more, preferably insulated, enclosures. The refrigeration may be used to cool, i.e. cool and/or freeze, articles such as food or pharmaceuticals. Such refrigeration can be effectively employed without the need for employing complicated vacuum operation.

[0025] The invention may be used to provide refrigeration required for cooling and/or freezing of food and pharmaceutical products, such as air make-up systems, cold room storage, blast freezers, and freezer applications conventionally employing mechanical freezers or cryogenic freezers. The invention may be used to provide refrigeration for all freezer types such as blast room, tunnel (stationary or conveyor), multi-tier, spiral

more components of the refrigerant mixture has a normal boiling point which differs by at least 5 degrees Kelvin, more preferably by at least 10 degrees Kelvin, and most preferably by at least 20 degrees Kelvin, from the normal boiling point of every other component in that refrigerant mixture. This enhances the effectiveness of providing refrigeration over a wide temperature range, particularly one which encompasses cryogenic temperatures. In a particularly preferred embodiment of the invention, the normal boiling point of the highest boiling component of the multicomponent refrigerant fluid is at least 50°K, preferably at least 100°K, most preferably at least 200°K, greater than the normal boiling point of the lowest boiling component of the multicomponent refrigerant fluid.

[0035] The components and their concentrations which make up the multicomponent refrigerant fluid useful in the practice of this invention are such as to form a variable load multicomponent refrigerant fluid and preferably maintain such a variable load characteristic throughout the entire temperature range of the method of the invention. This markedly enhances the efficiency with which the refrigeration can be generated and utilized over such a wide temperature range.

[0036] One preferred variable load multicomponent refrigerant fluid useful in the practice of this invention comprises two or more components from the group consisting of CF_4, CH_4 C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12}, i-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, C_2H_4, C_3H_6, C_4H_8, O_2, Ar, N_2, Ne and He.

[0037] The defined multicomponent refrigerant fluid of the invention is zeotropic. The components have different boiling points to span the entire temperature range of interest so that desired very low temperatures, such as cryogenic temperatures, can be achieved efficiently and generally with only a single stage of compression and without the need for vacuum operation. This contrasts with conventional refrigerants used to provide refrigeration which are composed of single components or blends of two or three components formulated to behave like a single component, i.e. narrow-boiling azeotropic or near-azeotropic blends.

[0038] The invention is employed to provide refrigeration to an enclosure, particularly an insulated enclosure. Such insulated enclosure used with the invention is typically a freezer, cold storage container or cold room. It need not be completely closed to the ambient atmosphere. Any insulation means which is effective in reducing heat leak into the container or freezer may be used. Under some limited circumstances, it may be that the subambient temperature facility, such as a cold processing room, is not insulated or is only partially insulated.

[0039] The invention will be described in greater detail with reference to the Drawings. Referring now to Figure 1, multicomponent refrigerant fluid 50 is compressed to a pressure generally within the range of from 30 to 1000 pounds per square inch absolute (psia), preferably from 100 to 600 psia, by passage through compressor 51 and resulting compressed multicomponent refrigerant fluid 52 is cooled of the heat of compression by passage through cooler 53. Resulting cooled multicomponent refrigerant fluid 54 is further cooled and at least partially, preferably completely, condensed by passage through heat exchanger 55. Resulting at least partially condensed multicomponent refrigerant fluid 56 is expanded through valve 57 to a pressure generally within the range of from 5 to 100 psia, preferably from 15 to 100 psia, thereby generating refrigeration by the Joule-Thomson effect, i.e. lowering of the fluid temperature due to pressure reduction at constant enthalpy. The expansion of the multicomponent refrigerant fluid through valve 57 may also cause some of the refrigerant fluid to vaporize. The pressure levels employed for the high pressure refrigerant of stream 52 and the low pressure refrigerant of stream 58, and the composition of the refrigerant, are selected to achieve the desired temperature levels at acceptable cost and efficiency.

[0040] Refrigeration bearing multicomponent refrigerant fluid 58 is then warmed and vaporized by passage through heat exchanger 55 and then passed as stream 50 to compressor 51 and the cycle begins anew. The warming and vaporization of the refrigeration bearing multicomponent refrigerant fluid in heat exchanger 55 serves to cool by indirect heat exchange refrigerant fluid 54, as was previously described, and also to cool by indirect heat exchange insulated enclosure atmosphere fluid, as will now be described.

[0041] A portion of the atmosphere fluid, which is typically air but may be another fluid such as nitrogen, carbon dioxide or any other suitable fluid, is withdrawn from insulated enclosure 59 in stream 60 and passed through separator 61 to remove any entrained ice. Separator 61 may be a centrifugal separator, a filter, or any other suitable separation means. Ice-free insulated enclosure atmosphere fluid 62 then flows through blower 63 which produces pressurized gas stream 64, generally at a pressure within the range of from 15 to 100 psia, preferably from 16 to 20 psia, and then through purification unit 25. If necessary, additional make up gas may be provided, such as is shown in Figure 1 by stream 68, compressed in blower 69, passed in stream 70 through purification unit 71 and then as stream 72 combined with stream 64 to form stream 65. Purification units 25 and 71 may be molecular sieve, adsorption bed, or any other suitable means for removing high boiling components such as moisture or carbon dioxide. Alternatively, all of the fluid to be refrigerated may be obtained by means of stream 68 such that fluid removed from enclosure 59 is not recirculated.

[0042] Fluid 65 is then passed through heat exchanger 55 wherein it is cooled by indirect heat exchange with the aforesaid warming and vaporizing multicomponent refrigerant fluid resulting in the production of refrigerated insulated enclosure atmosphere fluid 66 which typically has a temperature less than 250°K and generally

111, which may be a two-phase stream, is warmed and preferably at least partially vaporized by passage through heat exchanger 107, thereby serving to cool by indirect heat exchange aforesaid steam 108 as well as insulated enclosure atmosphere fluid which is passed to heat exchanger 107 in stream 112. The resulting refrigerated insulated enclosure atmosphere fluid, generally at a temperature within the range of from -30°F to -50°F, is passed in stream 113 from heat exchanger 107 to an insulated enclosure (not shown) wherein the refrigeration within stream 113 is provided and employed.

[0050] Warmed multicomponent refrigerant fluid is passed from heat exchanger 107 in stream 106 through heat exchanger 105 wherein it is further warmed and from there in stream 101 through heat exchanger 99 wherein it is further warmed and preferably further vaporized by indirect heat exchange with aforesaid cooling stream 100 and also with insulated enclosure atmosphere fluid which is passed to heat exchanger 99 in stream 102. The resulting refrigerated insulated enclosure atmosphere fluid, generally at a temperature within the range of from 0°F to -20°F, is passed in stream 103 from heat exchanger 99 to an insulated enclosure (not shown) wherein the refrigeration within stream 103 is provided and employed. The resulting further warmed multicomponent refrigerant fluid is passed from heat exchanger 99 in stream 98 through heat exchanger 97 and then as stream 92 to mixer 20 wherein it mixes with stream 91 to form stream 93 for further processing as previously described.

[0051] Figure 4 illustrates another preferred embodiment of the invention wherein the multicomponent refrigerant fluid is used to provide refrigeration at more than one temperature level and thus can provide refrigeration to more than one insulated enclosure. The embodiment of the invention illustrated in Figure 4 employs more than one phase separation of the multicomponent refrigerant fluid.

[0052] Referring now to Figure 4, multicomponent refrigerant fluid 200 is compressed by passage through compressor 201 to a pressure generally within the range of from 30 to 300 psia, and resulting compressed multicomponent refrigerant fluid 202 is cooled of the heat of compression by passage through cooler 203. Resulting multicomponent refrigerant fluid 204 is further compressed by passage through compressor 205 to a pressure generally within the range of from 60 to 600 psia, and resulting compressed multicomponent refrigerant fluid 206 is cooled and partially condensed by passage through cooler 207. Two-phase multicomponent refrigerant fluid from cooler 207 is passed in stream 208 to phase separator 209 wherein it is separated into vapor and liquid portions. Since multicomponent refrigerant fluid 200 is a zeotropic mixture, the composition of these vapor and liquid portions differ. Preferably, the liquid portion contains substantially all of the highest boiling component of multicomponent refrigerant fluid 200 and the vapor portion contains substantially all of the lowest boiling component of multicomponent refrigerant fluid 200.

[0053] The liquid portion of the multicomponent refrigerant fluid is passed from phase separator 209 in stream 211 through heat exchanger 212 wherein it is subcooled. Resulting subcooled liquid stream 213 is expanded through valve 214 to generate refrigeration by the Joule-Thomson effect. Resulting refrigeration bearing multicomponent refrigerant fluid 215, which is generally at a pressure within the range of from 15 to 100 psia, is passed through mixing device 21 and then in stream 217 through heat exchanger 212 wherein it is warmed and completely vaporized by indirect heat exchange with insulated enclosure atmosphere fluid and then passed in stream 200 to compressor 201 for a new cycle. The insulated enclosure atmosphere fluid, is passed to heat exchanger 212 in stream 218 and the resulting refrigerated insulated enclosure atmosphere fluid, generally at a temperature within the range of from 30°F to 60°F, is passed in stream 219 from heat exchanger 212 to an insulated enclosure (not shown) wherein the refrigeration within stream 219 is provided and employed.

[0054] The vapor portion of the multicomponent refrigerant fluid is passed from phase separator 209 in stream 210 through heat exchanger 212 wherein it is cooled by indirect heat exchange with warming fluid in stream 217 and then passed in stream 220 to intermediate heat exchanger 221 for further cooling. In one or both of the cooling steps in heat exchanger 212 and 221 a portion of the multicomponent refrigerant fluid is condensed so that multicomponent refrigerant fluid 223 from heat exchanger 221 is a two-phase stream. Stream 223 is passed to phase separator 224 wherein it is separated into vapor and liquid portions.

[0055] The liquid portion from phase separator 224 is passed in stream 226 through heat exchanger 227 wherein it is subcooled. Resulting subcooled liquid stream 228 is expanded through valve 229 to generate refrigeration by the Joule-Thomson effect. Resulting refrigeration bearing multicomponent refrigerant fluid 230, which is generally at a pressure within the range of from 15 to 100 psia, is passed though mixing device 22 and then in stream 232 through heat exchanger 227 wherein it is warmed and vaporized by indirect heat exchange with insulated enclosure atmosphere fluid. The insulated enclosure atmosphere fluid is passed to heat exchanger 227 in stream 233 and the resulting refrigerated insulated enclosure atmosphere fluid, generally at a temperature within the range of from -70°F to -110°F, is passed in stream 234 from heat exchanger 227 to an insulated enclosure (not shown) wherein the refrigeration within stream 234 is provided and employed. Warmed multicomponent refrigerant fluid from heat exchanger 227 is passed in stream 222 through heat exchanger 221 for warming by indirect heat exchange with cooling stream 220 and from there in stream 216 to mixer 21 wherein it mixes with stream 215 to form stream 217 for further processing as previously described.

ing of hydrocarbons, fluorocarbons, hydrofluorocarbons, fluoroethers and atmospheric gases;
(B) cooling and at least partially condensing the compressed multicomponent refrigerant fluid;
(C) expanding the at least partially condensed multicomponent refrigerant fluid to generate refrigeration; and
(D) warming and at least partially vaporizing the refrigeration bearing multicomponent refrigerant fluid and employing refrigeration from the multicomponent refrigerant fluid in an enclosure.

2. The method of claim 1 wherein the refrigeration is employed for cooling or freezing food.

3. The method of claim 1 wherein the warming and at least partially vaporizing of refrigeration bearing multicomponent refrigerant fluid is by heat exchange with insulated enclosure atmosphere fluid to produce refrigerated insulated enclosure atmosphere fluid and further comprising (E) employing the refrigerated insulated enclosure atmosphere fluid within an insulated enclosure to provide refrigeration to the insulated enclosure.

4. The method of claim 3 wherein the heat exchange between the refrigeration bearing multicomponent refrigerant fluid and the insulated enclosure atmosphere fluid takes place outside the insulated enclosure.

5. The method of claim 3 wherein the heat exchange between the refrigeration bearing multicomponent refrigerant fluid and the insulated enclosure atmosphere fluid takes place within the insulated enclosure.

6. The method of claim 3 wherein the cooling of the multicomponent refrigerant fluid in step (B) partially condenses the multicomponent refrigerant fluid and the resulting liquid is employed to carry to steps (C), (D) and (E); further comprising (F) cooling the resulting vapor to produce cooled fluid, expanding the cooled fluid to generate refrigeration, and warming the resulting refrigeration bearing fluid to produce refrigerated fluid for use in an insulated enclosure.

7. The method of claim 3 wherein the cooling of the multicomponent refrigerant fluid in step (B) partially condenses the multicomponent refrigerant fluid and the resulting liquid is employed to carry out steps (C), (D) and (E); further comprising (G) partially condensing the resulting vapor to produce a liquid fluid and a vapor fluid, expanding the liquid fluid to generate refrigeration and warming the resulting refrigeration bearing liquid fluid to produce refrigerated fluid for use in an insulated enclosure; and (H) at least partially condensing the vapor fluid and expanding the at least partially condensed fluid to generate refrigeration, and warming the resulting refrigeration bearing fluid to produce refrigerated fluid for use in an insulated enclosure.

8. The method of claim 1 wherein the multicomponent refrigerant fluid consists solely of hydrocarbons.

9. The method of claim 1 wherein the multicomponent refrigerant fluid comprises at least one atmospheric gas.

10. The method of claim 1 wherein the multicomponent refrigerant fluid comprises at least two components from the group consisting of CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}, n-C_5H_{12}, i-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, C_2H_4, C_3H_6, C_4H_8, CF_4, O_2, Ar, N_2, Ne and He.

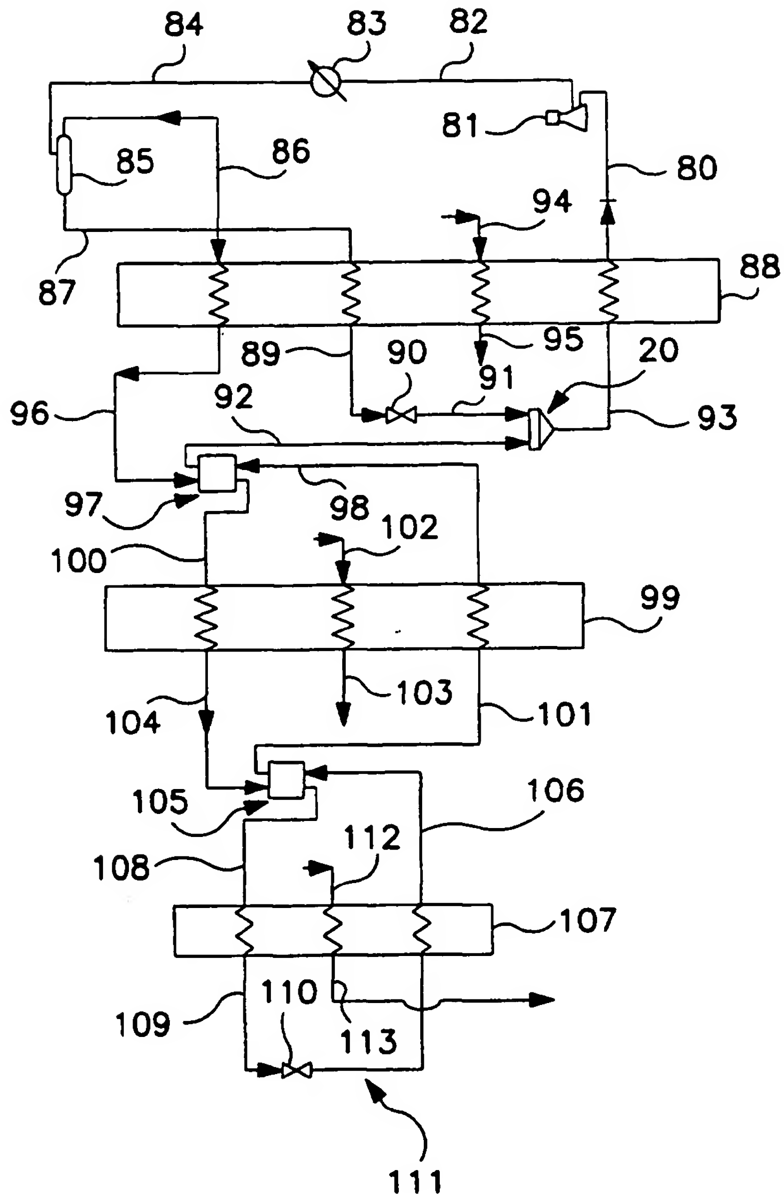
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FIG. 3

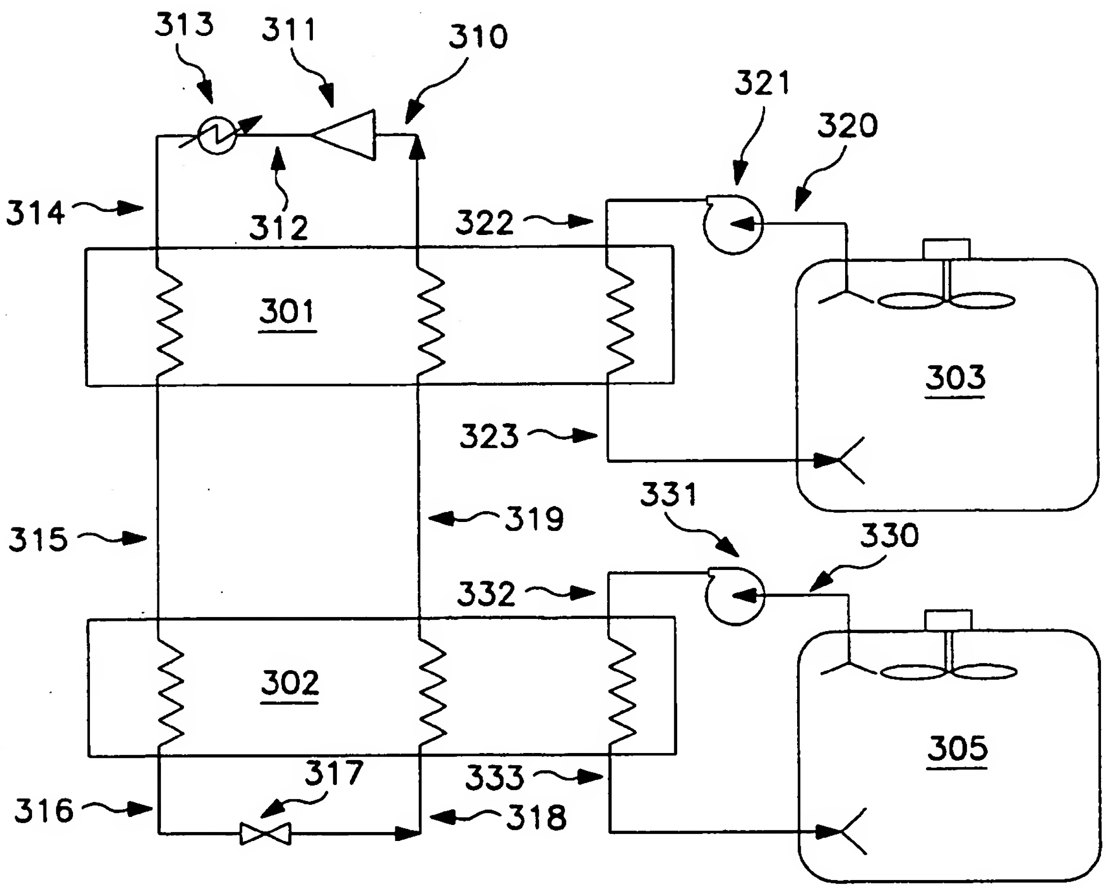
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FIG. 5

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 01 11 5467

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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